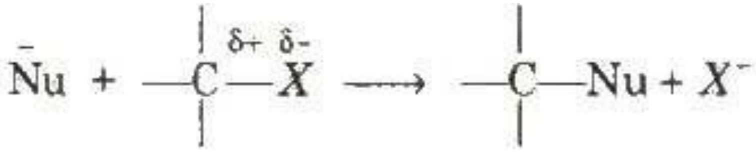
CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED REVISION NOTES OF CHAPTER -10)
GANESH KUMAR DATE:- 10/03/2021

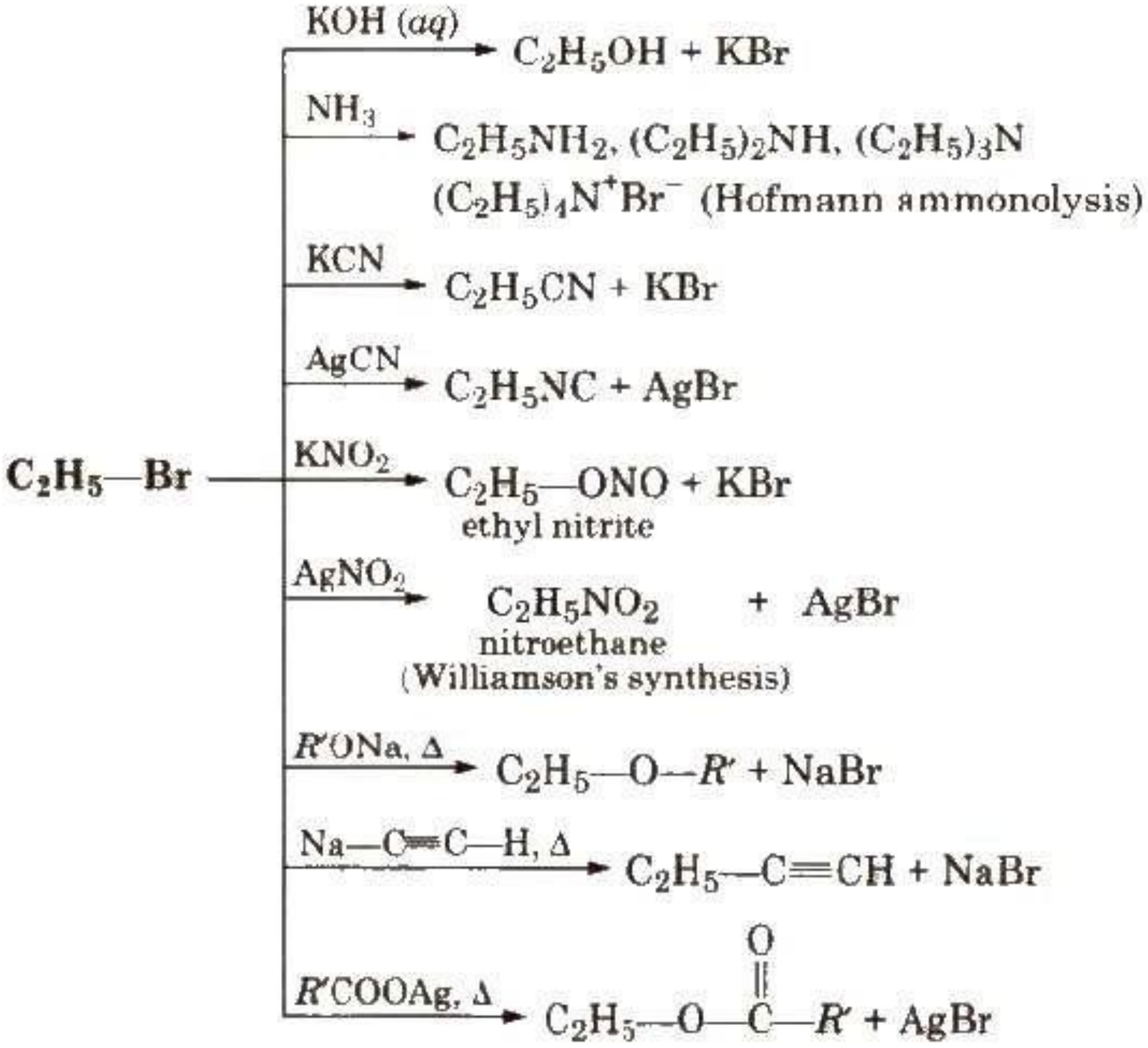
Haloalkanes and Haloarenes

Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)



$$\overset{-}{Nu} + -\overset{|}{\underset{|}{C}}{}^{\delta+}-X^{\delta-} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^-$$

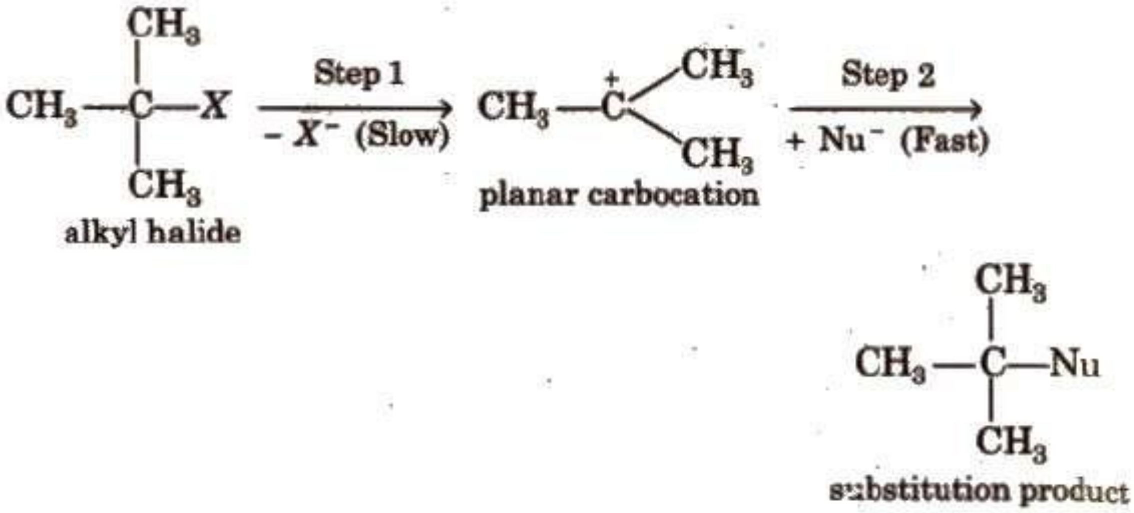


KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO_2 form R-ONO while $AgNO_2$ produces R-NO_2 as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) S_N1 type (Unimolecular nucleophilic reactions proceed in two steps:

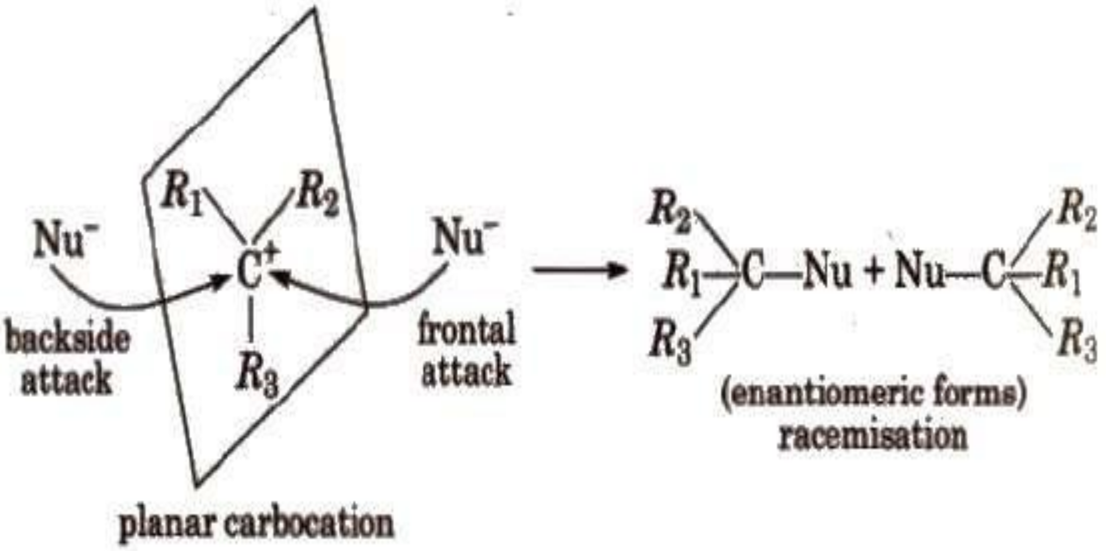


Rate, r = k [RX). It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism 3° > 2° > 1°

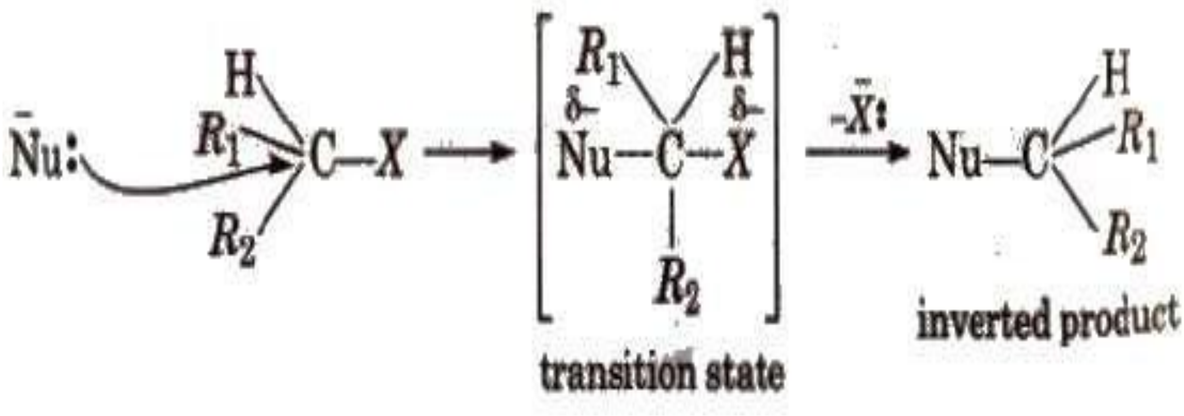
Polar solvents, low concentration of nucleophiles and weak nucleophiles favour

S_N1 mechanism. In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) S_N2 type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with r = k[RX] [Nu].

During S_N2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards S_N2
mechanism is 1° > 2° > 3°

Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$:CN^- > :I^- > :OR^- > :OH^- > CH^3COO: > H_2O > F^-$

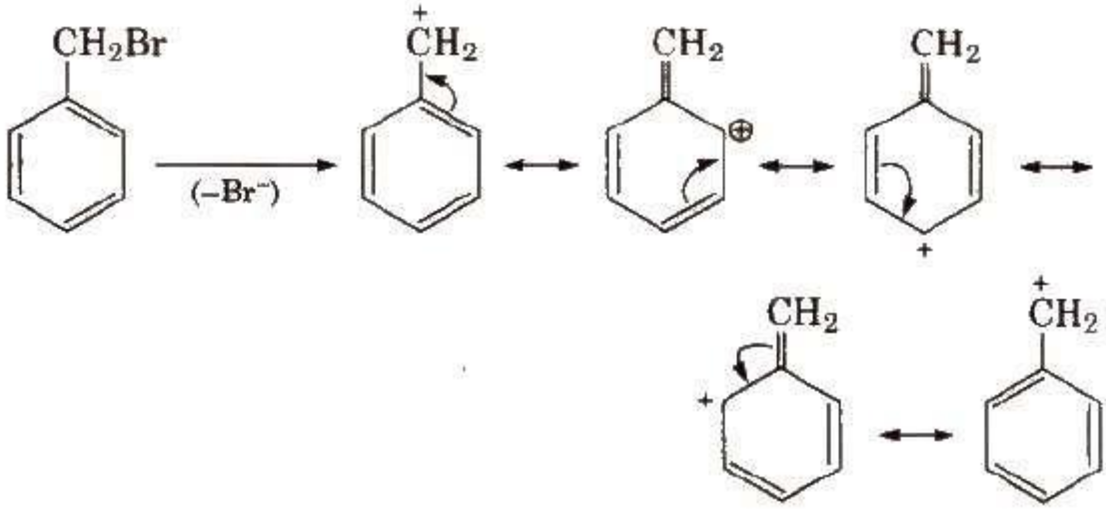
Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order

$$S_N1 : (CH_3)_3CX > C_6H_5—CH_2—X > CH_2{=}CH—CH_2X$$
$$> (CH_3)_2CHX > CH_3CH_2X > CH_3X$$

$$S_N2 : \underbrace{C_6H_5CH_2X > CH_2{=}CH—CH_2X}_{\text{resonance stabilised}} > CH_3X$$
$$> CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$$

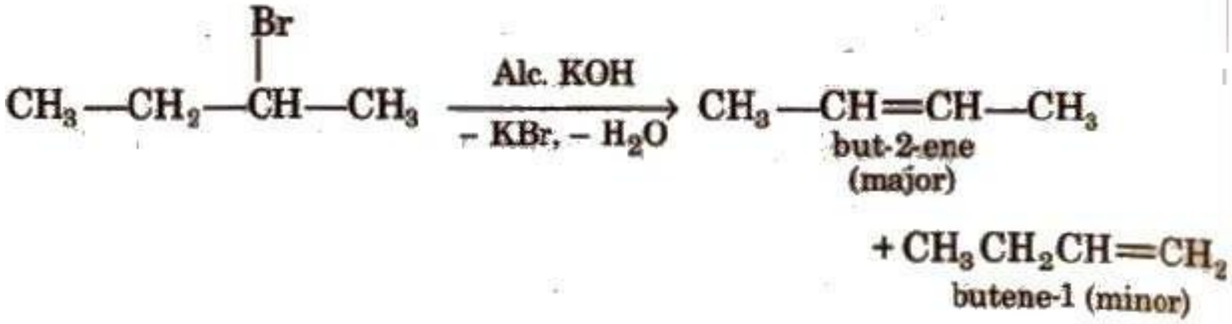
Resonating structure of benzyl carbocations are



Relative reactivity of alkyl halides for same alkyl
group is RI > RBr > RCl > RF

2. Elimination Reactions

Dehydrohalogenation is a β – elimination reaction in which halogen is from α-carbon atom and the hydrogen from the α-carbon according to Saytzeff rule, e.g.,



$$CH_3-CH_2-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow[-\,KBr,\ -\,H_2O]{Alc.\ KOH} \underset{\substack{\text{but-2-ene}\\ \text{(major)}}}{CH_3-CH=CH-CH_3} + \underset{\text{butene-1 (minor)}}{CH_3CH_2CH=CH_2}$$

Ease of dehydrohalogenation among halides 3° > 2° > 1°

i.e., $(CH_3)_3CCl > (CH_3)_2CHCl > CH_3CH_2Cl$

3. Reduction

$$C_2H_5-Br + H_2 \xrightarrow{Ni,\ 575\ K} C_2H_6 + HBr$$

$$C_2H_5I + HI \xrightarrow{Red\ P,\ 420\ K} C_2H_6 + I_2$$

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